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## (54) Production of aromatics from alkanes

(57) In a process for conversion of C<sub>2</sub>-C<sub>6</sub> alkanes to aromatics over a zeolite, the improvement resides in the separation in situ of by-product hydrogen formed in the reaction by means of a membrane provided in the reactor. By this process the yield of aromatics is improved.

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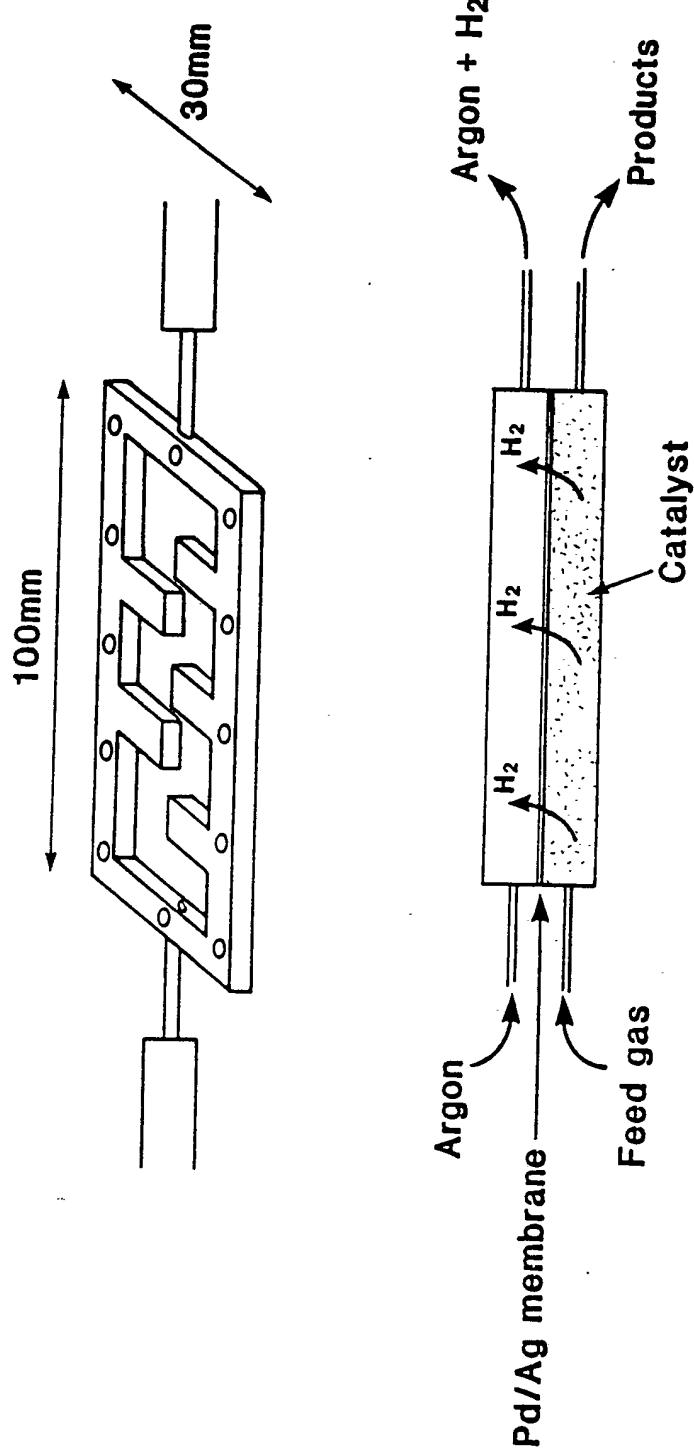


Fig 1 The H<sub>2</sub> separation reactor

## SPECIFICATION

## Improved synthesis of aromatics from alkanes

5 The present invention relates to an improved process for producing aromatic hydrocarbons by dehydrocyclodimerisation (DHCD) of an alkane over a catalyst. 5

During the DHCD of an alkane e.g. propane over a catalyst e.g. as claimed and described in our prior patents, hydrogen is an inevitable by-product. In such a system the presence of hydrogen promotes hydrocracking and thereby results in loss in selectivity to and yield of the 10 desired aromatics. 10

It is an object of the present invention to remove in-situ by-product hydrogen formed during the DHCD reaction thereby improving the selectivity to and yield of aromatics.

Accordingly, the present invention is a process for catalytic dehydrocyclodimerisation of C<sub>2</sub>-C<sub>6</sub> alkanes to a mixture of aromatic hydrocarbons and by-product hydrogen in a reactor characterised in that the reactor is provided with a membrane capable of selective, in-situ transfer of at 15 least a portion of the hydrogen in the mixture across the membrane. 15

The C<sub>2</sub>-C<sub>6</sub> alkane which is subjected to DHCD is suitably a C<sub>2</sub>-C<sub>4</sub> alkane i.e. ethane, propane, a butane or mixtures thereof, preferably ethane or propane.

As stated above processes for producing aromatic hydrocarbons by DHCD of an alkane over a 20 catalyst are well known. The process preferably uses a catalyst composition comprising a zeolite of the MFI type in its hydrogen form loaded with a gallium compound e.g. gallium oxide. The catalyst composition can include a binder such as silica or alumina, preferably silica for the gallium/MFI catalyst. The amount of gallium present in the gallium/MFI catalyst is suitably from 0.1-10% by weight of gallium metal. 20

25 The gallium/MFI catalyst is suitably activated by calcination or steaming. Where steaming is used, the catalyst is steamed in an oxidising atmosphere e.g. a 15% steam in air at an elevated temperature suitably from 400° to 750°C, preferably from 450°, to 650°C e.g. 550°C prior to being contacted with the alkane feed in the reaction system. After steam treatment but before contact with the alkane feed the catalyst is suitably activated in a reducing atmosphere e.g. 30 hydrogen at elevated temperature suitably from 400° to 700°C, preferably from 450° to 650°C, e.g. 500°C. 30

The gallium/MFI catalyst after activation is suitably brought into contact with the alkane feed at elevated temperature suitably from 400° to 650°C, preferably from 450° to 625°C, e.g. 500°C in a reactor.

35 The DHCD reaction is suitably carried out at a temperature from 450° to 650°C, preferably from 475° to 575°C; a pressure from 1 to 20 bar, preferably from 1 to 10 bar; and a WHSV from 0.2 to 5, preferably from 0.5 to 3.0. 35

The reactor is fitted with a membrane which is capable of selectively transferring at least a portion of hydrogen in the gaseous mixture of reaction products in-situ across the membrane 40 thereby separating the hydrogen. The membrane is suitably made from the following metals or their alloys: Pd, Ti, Zr, Ni, Co, Fe, Pt, V, Nb, Ta and Ag. The membrane is preferably made from a palladium-silver alloy (76% Pd/24% Ag w/w). A schematic representation of one particular design of reactor is shown in the accompanying drawing. The thickness of the membrane is suitably from 0.01 to 0.5 mm; preferably from 0.01 to 0.1 mm. The membrane is fitted in the 45 reactor in such a way that it splits the reactor into two compartments. In one compartment the catalyst is placed and the alkane feed allowed to pass over it. In the other compartment a steady flow of a gas inert under the reaction conditions e.g. argon or nitrogen is maintained. This inert gas flow is maintained relatively high so that it rapidly carried away any diffused 50 hydrogen thereby maintaining a hydrogen partial pressure difference across the membrane and hence facilitating the removal of a substantial portion of the hydrogen in the mixture of reaction products. 50

In operation, as shown in the accompanying drawing, feed gases are passed through one side of the reactor in which the catalyst is placed. Hydrogen by-product is evolved as the reaction proceeds and selectively diffuses across the membrane. On the other side of the membrane the 55 hydrogen by-product is rapidly swept away by the steady flow of argon so as to maintain as high a difference in hydrogen partial pressure across the membrane as is possible. 55

The liquid products of the reaction were isolated and analysed by gas chromatography.

The process carried out in a reaction system with a membrane for selective, in-situ removal of hydrogen showed an increased selectivity and thereby resulting in higher yield of aromatic 60 hydrocarbons. Also, the formation of unwanted methane is significantly reduced. 60

The present invention is further illustrated with reference to the following Examples and Comparative Tests.

A reactor made from 6 mm stainless steel plate and fitted with a Pd/Ag alloy membrane was designated and constructed. The hydrogen membrane is 0.1 mm thick, made from 76% Pd/24% Ag. A diagram of this reactor is given in Fig. 1. The upper drawing shows one half of the reactor. The whole consists of two similar halves between which fits the membrane, as shown 5 in the lower drawing. The protrusions in each half of the reactor provide increased tortuosity and help support the membrane. A thermocouple pocket was drilled into the reactor side to allow 5 temperature measurement. The reactor was placed in a cylindrical furnace on an atmospheric pressure lab-rig for the experiments. The mode of operation is shown in the lower diagram of Fig. 1. Feed gas passes through one side of the reactor, in which the catalyst sits. Hydrogen is 10 evolved as reaction proceeds which can then selectively diffuse across the membrane. On the other side of the membrane a very high flow of argon is maintained to rapidly carry away the 10 hydrogen and so maintain as high a difference in hydrogen partial pressure across the membrane as possible.

15 2. *Propane DHCD*

The zeolite used in the catalyst was prepared from an ammonia based MFI zeolite with a silica to alumina ratio of 36:1 (prepared according to the general process described in our published EP-A-0030811). This zeolite was acid washed with 8.75% nitric acid, ammonium exchanged twice using a 1M ammonium nitrate solution and then loaded with gallium using 0.0056 g/ml 20 gallium nitrate solution to form the catalyst. After binding the catalyst with silica using "Ludox" AS 40 (Regd Trade Mark) silica, crushing and sieving to 12/30 mesh BSS, the resultant catalyst 20 granules were steamed in 16% steam/air at 550°C for 2 hours. Activation consisted of heating under flowing nitrogen, before introducing hydrogen for 1.5 hours at 500°C. After reduction, feed was introduced at 1.7 WHSV, 500°C. The test period lasted from 0.5 to 1.5 hours on 25 stream, over which period gas samples were collected and the liquid product collected and weighed. Analysis of both liquids and gases was by off-line gas chromatography. Hydrogen diffusion was measured both by difference in argon flowrate and by collecting gas samples and analysing by gas chromatography for vol% hydrogen.

Nitrogen was re-introduced after the test period and the procedure repeated at a number of 30 different temperatures, using the same catalyst, without regeneration and without further reduction between runs. The temperatures used were (in order) 475, 450, 535, 550°C. All results are presented in a form including the diffused hydrogen in the reaction products (hydrogen taken as 30 total hydrogen).

Comparison experiments (standard) were carried out, in the absence of hydrogen removal, 35 using a standard quartz reactor in a similar atmospheric lab-rig. The same activation procedure and experimental sequence were followed as were used for the membrane reactor experiments. The only difference was that here a catalyst charge of 4.3 g was used, compared to 2.4 g for the membrane reactor, though WHSV's and contact times were similar in each case.

The results are tabulated below:-

TABLE  
PROPANE CONVERSION AT 1 BAR

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Temp (°C)	Reactor	WHSV (hr <sup>-1</sup> )	C <sub>3</sub> <sup>+</sup> Conv	SEL Aro	SEL CH <sub>4</sub>	SEL C <sub>2</sub> <sup>+</sup>	SEL H <sub>2</sub>	ARO Yield	PCA/ ARO	Mass Balance
450	Standard	1.76	19.6	53.4	14.5	12.3	6.4	10.4	5.9	96.6
	Membrane	1.70	21.6	56.4	12.0	12.5	7.8	12.2	4.9	97.3
475	Standard	1.77	36.4	58.4	17.0	11.4	6.0	21.3	7.0	97.2
	Membrane	1.68	40.3	62.4	14.4	11.3	6.6	25.1	6.9	95.4
500	Standard	1.79	56.2	57.8	19.1	12.9	5.9	32.5	10.4	95.4
	Membrane	1.63	57.6	65.8	13.4	10.9	6.9	37.9	10.0	102.1
535	Standard	1.78	82.6	60.3	20.9	8.8	6.0	49.8	(10.7)	89.3
	Membrane	1.69	78.3	64.1	17.3	9.0	6.3	50.2	13.7	101.8
550	Standard	1.77	89.1	53.2	18.9	15.7	5.6	47.4	11.3	93.6
	Membrane	1.67	87.0	63.6	17.9	8.7	6.2	55.3	13.8	101.6

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**Notes:**

Conversions, selectivities and yields are all on a wt% basis.

C<sub>3</sub><sup>+</sup> = PropaneC<sub>2</sub><sup>+</sup> = Ethane

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**CLAIMS**

1. A process for catalytic dehydrocyclodimerisation (DHCD) of C<sub>2</sub>-C<sub>6</sub> alkanes to a mixture of aromatic hydrocarbons and by-product hydrogen in a reactor characterised in that the reactor is provided with a membrane capable of selective, in situ transfer of at least a portion of hydrogen in the mixture across the membrane.

2. A process according to claim 1 wherein the C<sub>2</sub>-C<sub>6</sub> alkane is ethane, propane, a butane or mixtures thereof.

3. A process according to claim 1 or 2 wherein the DHCD catalyst is an MFI zeolite loaded with a gallium compound.

4. A process according to any one of the preceding claims wherein the DHCD is carried out at a temperature from 450-650°C, a pressure from 1-20 bar and a WHSV from 0.2-5.

5. A process according to any one of the preceding claims wherein the membrane consists essentially of one or more metals selected from Pd, Ti, Zr, Ni, Co, Fe, Pt, V, Nb, Ta, Ag and alloys thereof.

6. A process according to any one of the preceding claims wherein the membrane comprises a palladium-silver alloy.

7. A process according to any one of the preceding claims wherein the thickness of the membrane is from 0.01-0.5 mm.

8. A process according to any one of the preceding claims wherein the membrane is positioned in the reactor so as to split the reactor into two compartments.

9. A process according to claim 8 wherein one of the two compartments contains the DHCD catalyst and the other compartment is provided with means for sweeping the transferred hydrogen out of the reactor by a steady flow of a gas inert under the reaction conditions.

10. A process according to claim 9 wherein the transferred hydrogen is swept out of the reactor rapidly to maintain a hydrogen partial pressure difference across the membrane.

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11. A process for selectively transferring hydrogen in situ from a mixture of products according to claim 1 as hereinbefore described with reference to the Examples and Fig. 1.

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